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Luminescence From Gamma Irradiated Saccharides

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Abstract : The luminescent decay times and its dependence on different parameters (*viz.*, radiation dose, solvent temperature and mass of the solute) of γ-irradiated saccharides (glucose, mannose, lactose, maltose and trehalose dihydrate) have been studied by employing photon counting technique. It is observed that all the saccharides show three decay components throughout the temperature and mass range for all the doses studied. It is also seen that the decay times and their corresponding intensities do not depend on radiation dose, but all the decay times depend severely on temperature of the solvent and mass of the solute. Attempts have been made to correlate the findings with free radical formation and recombination, rate of dissolution, persistence of structure and electron spin resonance (ESR) measurements.

Keywords : Lyoluminescence, saccharide, free radical, decay, decay time

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1. Introduction

Crystalline saccharide powders when exposed to ionising radiations, free radicals are formed and thereby energy is stored in their crystal matrix. When these irradiated solids are dissolved in some suitable solvents, they proceed through a chain reaction and emit light [1]. This phenomenon is known as lyoluminescence (LL). This has been first reported by Ahnström and Ehrenstein [2].

Lyoluminescence has been observed in many categories of compounds and found useful application in radiation dosimetry. Lyoluminescent phosphors made of saccharides, proteins or amino acids are considered to be tissue equivalent due to their similar atomic composition. Hence LL can be applied

to personal dosimetry, radiation therapy, food preservation, sterilization of medical products etc., *i.e.*, in various fields where dose estimation is required [3].

Any ionising radiation irradiating saccharide powders generates free radicals. These trapped free radicals remain relatively stable in the crystalline matrix. However, their number may fade since they can undergo certain transformation, e.g. oxidation by atmospheric oxygen diffusing through the solid. It has been observed that only a small amount of fading results after prolonged storage [4,5]. So, saccharides can be safely taken for LL dosimetry.

On contact with a suitable solvent an irradiated saccharide releases the free radicals and ultimately decay by emitting light. According to Ahnström, there exists atleast two components of emitted light, one of them having a longer decay time, probably caused by peroxide reactions [6]. The radiation induced free-radical basis of LL in sugars has been investigated by ESR-correlation studies and found to agree within 5% in the range from 50 to 1000 Gy [7].

A large number of interesting work has been carried out on LL [1,8] and it has been found that various factors influence the light emission process in LL, *viz.*, pH of the solvent, mass of the solute, radiation dose, solvent temperature etc. The actual mechanism of LL is not clear and is still open for further investigation.

The free radical recombination reaction causes light emission during dissolution. The rate of change of LL intensity gives rise to decay spectrum characteristic of the material. The decay times of LL spectra not only serve as an additional parameter related to the phenomenon but also the knowledge of it will enable one to choose the proper time of data acquisition when measurement of the integrated yield is desired.

For dose measurement by LL technique, it is necessary to have a complete knowledge of the decay time of the material, the mass of the solute and the pH and temperature of the solvent to achieved a reproducible result. The present paper describes the measurements on the decay time of five saccharides, *viz.*, mannose, glucose, maltose, lactose and trehalose dihydrate. The dependence of decay times on different parameter, *viz.*, radiation dose, solvent

temperature and mass of the solute has been studied. An attempt has been made to correlate the findings with free radical formation and recombination, rate of dissolution, persistence of structure and ESR measurements.

2. Experimental

2.1 LL decay time measurements :

The LL reader fabricated for this purpose is of solvent injection type fitted with a Hamamatsu R1307 bialkali photomultiplier tube (PMT) and necessary electronics. The details of this reader which incorporates a photon counting facility for decay time measurement has been described elsewhere [9].

Measurements have been carried out on ^{60}Co γ-ray irradiated powdered (grain size 100 - 250 μm) glucose (E. Merck, Bombay), mannose, lactose, maltose and trehalose dihydrate (SRL, Bombay). The sample is kept in a well cleaned glass vial placed on the window of the PMT inside the light-tight chamber of the reader. Two ml solvent (water) is poured onto the sample in each case by a conventional hypodermic syringe. The data is taken by a multichannel analyser operated in the multichannel scaling mode. The dwell time is fixed at 40 ms per channel in a 4K channel setting to ensure a total available data acquisition time of $\sim$ 164 s which has been found to be long enough to allow the LL-time-spectrum to return to the background level in case of these saccharides.

Samples (irradiated to three doses, *viz.*, 200, 550 and 1000 Gy) of mass 5 - 6 mg have been used to measure the decay times. Such a small quantity of a sample is chosen to ensure quick dissolution. The measurements have been conducted for each of the five saccharides of dose 1000 Gy for a solvent temperature range 10^{0}C - 90^{0}C and for various solute masses, *viz.*, 1 mg to 20 mg at room temperature to find the decay times at different temperatures and various sample masses respectively. The temperature of the solution is measured by a calibrated low heat capacity thermo-couple placed at the site of the sample. Doubly distilled water having a pH 6.8 has been used as solvent in all cases. The background subtracted and dead time corrected counts are then analysed by a multi-exponential fit using a computer program for extracting the decay times [10].

2.2 ESR measurements :

To explain the origin of decay components the ESR spectra of these samples have been recorded at the room temperature with the Varian E112 spectrometer. The normal spectrometer settings of the parameters for the operation in the X-band microwave frequencies are as follows : klystron frequency 9.45 GHz, magnetic field setting 3430 G (1 G = 10^{-4}T), RF field modulation 8 G, microwave power 5 mW, time constant 0.250 s, scan range 10 x 100 G. In each case the sample is taken in a quartz tube of diameter 3 mm and placed at the ESR cavity. The ESR spectra have been recorded with the help of a strip-chart recorder. 1,1-diphenyl 2-picrylhydrazyl (DPPH) is used as the standard sample whose spin concentration is known (1.53 x 10^{21} per mg).

3. Results and discussion

3.1 Effect of radiation dose on LL decay times :

A typical LL decay spectrum of lactose of mass 5.5 mg for a particular dose of 550 Gy at room temperature (25^0C) along with the background is shown in Figure 1. Decay curves for each of the five saccharides have been studied for three different doses, *viz.*, 200, 550 and 1000 Gy of same mass at room temperature. A computer analysis yields three decay components in each of the five saccharides studied. It is observed that the decay times and the corresponding intensities do not depend on radiation dose [10]. When a particular saccharide is exposed to higher radiation doses, the concentration of free radicals increases but the types of free radicals formed do not change. Since different decay components originate from free radical recombination, the decay times do not change with radiation dose imparted to the sample. The values of the deacy times and corresponding intensities measured at room temperature are given in Table 1.

3.2 Effect of solvent temperature on LL decay times :

The variation of all the three decay times of these five saccharides (mass 5-6 mg) for a dose of 1000 Gy with solvent temperature have been studied [11] and in Figure 2 the nature of variation for trehalose dihydrate is shown. It is observed that the decay times of all the three components in the saccharides studied decrease with increase in solvent temperature in an almost similar

manner, showing a faster rate upto $\sim 30^0$C and a much slower rate beyond.

Table 1. Measured decay times and the corresponding intensities (averaged over all the doses) of three components of saccharides studied.
sample weight : 5 - 6 mg; solvent : water, pH 6.8; temperature : 25^0C

Sample used	Decay times of the components (s)			Intensities (%)		
	1st (τ_1)	2nd (τ_2)	3rd (τ_3)	I_1	I_2	I_3
Glucose	0.13 ± 0.03	0.80 ± 0.08	4.51 ± 0.33	9	33	58
Mannose	0.52 ± 0.07	1.97 ± 0.13	8.25 ± 0.41	10	36	54
Maltose	0.34 ± 0.05	1.41 ± 0.11	6.23 ± 0.37	5	49	46
Lactose	0.42 ± 0.07	2.17 ± 0.17	12.48 ± 0.85	10	64	26
Trehalose $2H_2O$	0.39 ± 0.05	1.78 ± 0.12	10.72 ± 1.11	30	33	37

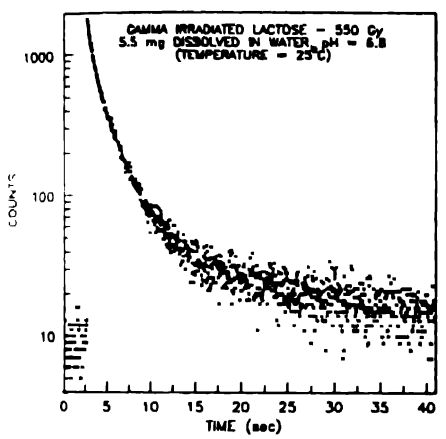

Figure 1. A typical experimental decay spectrum of lactose.

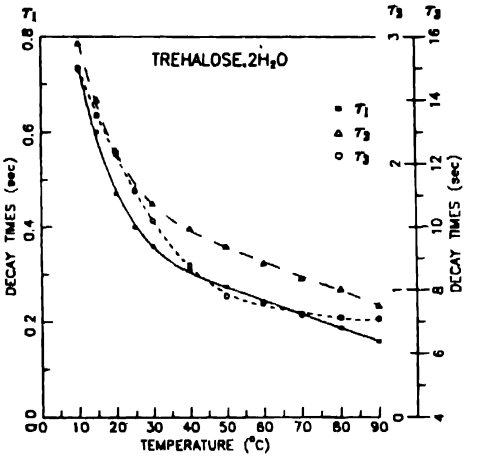

Figure 2. The variation of decay times with solvent (water, pH 6.8) temperature in trehalose dihydrate (1000 Gy).

The origin of the longest decay component (τ_3) is considered due to the persistence of some solute structure in the solution. With rise in solvent temperature the rate of dissolution increases and consequently the possibility of retaining that structure decreases. However, this increase is limited by the limiting value of solubility. This is why, above 50^0C, τ_3 does not change much unlike in the case of τ_1 and τ_2. At higher solvent temperatures the entrapped free radicals receive more energy and thus become capable of overcoming the potential barrier more readily. As a result, the free radical recombination rate enhances leading to reduction in the values of τ_1 and τ_2.

3.3 Effect of solute mass on LL decay times :

The variation of all these three decay times with various solute masses (1mg - 20 mg) at room temperature have been studied [12] and for maltose this variation is presented in Figure 3. It is observed that all the three decay components increase linearly with solute mass. The values of different decay times for 1 mg, 10 mg and 20 mg are given in Table 2.

In view of the fact that all the free radicals formed due to γ-ray irradiation in saccharides do not lose identity within a short time even after dissolution. It is expected that the decay time assumes longer values due to the persistence of structure in the solution as solute mass increases.

Table 2. Measured values of the three decay times for three different masse radiation dose : 1000 Gy ^{60}Co; solvent : water, pH 6.8; temperature : 25^0C

Sample used	1 mg			10 mg			20 mg		
	τ_1	τ_2	τ_3	τ_1	τ_2	τ_3	τ_1	τ_2	τ_3
Glucose	0.11	0.69	3.09	0.18	0.95	4.81	0.26	1.15	6.95
Mannose	0.24	0.90	4.95	0.90	3.00	13.0	1.66	5.86	21.0
Maltose	0.21	1.12	5.20	0.36	1.42	7.10	0.44	1.78	9.53
Lactose	0.19	1.50	5.80	0.41	2.12	20.0	0.70	2.66	34.98
Trehalose $2H_2O$	0.23	0.74	7.10	0.71	3.51	14.87	1.27	6.74	30.35

3.4 Nature of ESR spectra :

The first derivative ESR spectrum of mannose is shown in Figure 4. This ESR spectrum for mannose is very similar to that recorded by Bartlett and Brown

[13]. The absorption spectra obtained from derivative curves clearly indicate that the resonance is dominantly a doublet with a second weak absorption on the higher field side which signifies that at least two unpaired electron species are present in the sample. The g-values of the saccharides has been found to very close to that for DPPH, exhibits clear indication of localisation of the unpaired spin on carbon atom [10]. The prominant doublet of the dominant species is characteristic of the unpaired spin coupled with a single proton which may be found to attach itself with the carbon atom, the centre of the unpaired spin. It is also seen from the spectrum that the area under the curves is nearly proportional to the LL yield.

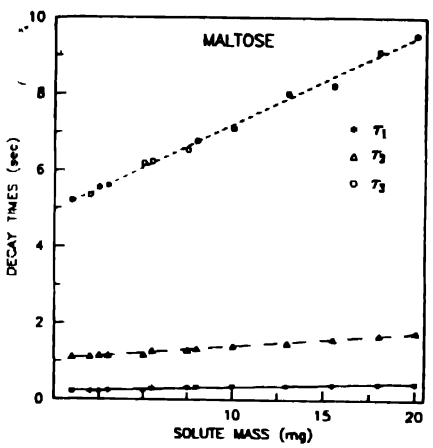

Figure 3. The variation of decay times with solute mass when dissolved in water (pH 6.8) for maltose (1000 Gy) at room temperature.

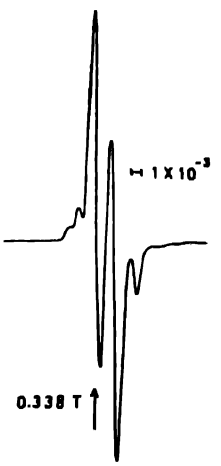

Figure 4. A first derivative ESR spectrum of mannose (^{60}C0 1000 Gy) at room temperature.

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